

“A New Coating Process for Production of Coated Magnesium Powders”

Scientific and Technical Report

Contract #: N00164-07-R-6068

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Executive Summary

This phase III project focused on the development of a pre-production scale process for the deposition of aluminophosphate coatings on 1-lb batches of magnesium powder to passivate the magnesium against moisture-induced degradation. Work conducted in the prior Phase II effort was successful in the development of a laboratory-scale coating process for 30g batches of atomized magnesium powder. This work focused on two primary tasks: 1) development of the coating process to provide protection for ground magnesium powder similar to that achieved for atomized material in Phase II, and 2) increase the batch size to demonstrate feasibility of production and to provide larger quantities of material for validation and testing.

Four primary areas of focus in the project were:

- 1) Installation and set-up of coating equipment and supporting infrastructure
- 2) Coating process development for the deposition of high-quality coatings on ground and atomized magnesium powder in 1-lb batches
- 3) Characterization and evaluation of performance for 1-lb batches of coated magnesium
- 4) Production and delivery of 55 pounds of coated magnesium powder of three atomized and one ground powder types

During this project, a coating system suitable for the deposition of the Cerablak®-based coating on 1-lb batches of powder was installed, and the supporting infrastructure was designed and constructed. Process parameters for the coating deposition were developed in order to achieve high-quality coatings on both atomized and ground magnesium powder. A strong effort was oriented toward the adaptation of the coating process for the ground magnesium powder, and a major improvement in the performance of coated ground magnesium powder against moisture-induced degradation was achieved.

Powder produced as deliverable for this project was characterized for metallic magnesium content, magnesium hydroxide content, and performance against humidity-based aging. Coated atomized powders showed little or no reduction in metallic magnesium content during coating and decreased magnesium hydroxide content compared to the uncoated powder of the same type. Performance of atomized powder in humidity-based aging showed reduced hydroxide formation compared to uncoated powder for a given exposure, and fine-mesh powders showed the greatest improvement in performance with a rate of degradation less than one half that of the uncoated material.

The performance of coated ground magnesium powder, RMC-200BS, was dramatically improved during this project. Performance against humidity-based aging shows a highly stable initial period that is not present with uncoated ground magnesium. Although analysis of the as-coated ground powder shows a small residual content of magnesium hydroxide, on the order of 3 wt%, there appears to be little other loss of metallic magnesium due to the coating process. Under the accelerated aging conditions used in this work, uncoated ground magnesium rapidly degraded to a hydroxide content exceeding that of the coated material, and the coated material maintained a highly stable hydroxide level for over twice that period of time. This should provide increased shelf-life and minimize losses in combustion reliability.

The final deliverable containing 10 lb of coated -325 mesh atomized powder, 5 lb of coated 200/325 mesh atomized powder, 15 lb of coated Gran 16 atomized powder, and 25 lb of coated RMC-200BS ground magnesium powder was produced and delivered at the conclusion of this work.

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Overview

Issues related to the interaction of moisture with magnesium-based pyrotechnic compositions have historically been a problem. The interaction results in the loss of metallic magnesium available for combustion and the production of hydrogen gas as a by-product that presents a potential hazard for inadvertent ignition. ATFI developed a laboratory-scale phosphate-based inorganic coating for the protection of magnesium from moisture during a previous Phase II project which showed promise for atomized magnesium powder. This Phase III project sought to increase the batch size from the previous lab-scale 30g batch to a pre-production 1-lb batch size and to extend the protection to ground magnesium powder as well as atomized.

This scientific and technical report covers the work carried out during the originally specified 6 month period of performance from July 6, 2007 through January 6, 2008 and during the no-cost extension from January 6, 2008 through April 6, 2008. The work performed under this project is documented according to the project tasks as outlined in the contract and outlined in the task plan below (see Table 1). In brief, Task 1 involved the construction and assembly of the coating system and supporting infrastructure, which was used for the scale-up and production of 1-lb batches of coated magnesium powder. Task 2 focused on the process development required to scale batch sizes from the Phase II batch size of 30g to the desired pre-production batch size of 1-lb. The powder produced in task 2 was analyzed in task 3 to determine the characteristics of the as-coated material and the moisture-induced aging behavior. Finally, task 4 focused on the delivery of the 1-lb batches of coated magnesium, which constituted the final deliverable of the Phase III project.

During the course of the original period of performance, initial 1-lb batches of each powder type were prepared at the end of the scale-up process, Task 2. A 3-month no-cost extension was requested in order to characterize the aging behavior of those powders over a time sufficient to benchmark their performance and provide a baseline for the production batches. During this time a strong effort was also placed on improvement of the performance of coated ground magnesium, and a major improvement of performance was achieved.

The final deliverable, 55lbs of coated magnesium powder, was shipped to NSWCC Crane on March 31, 2008.

Table 1: Project task plan and schedule

Task	Jul- Aug	Sep- Oct	Nov- Dec
1.0 Identify, Operate, and Optimize Equipment for Increased Batch Size	←→		
2.0 Scale-up of Batch Size for New Coating Process up to 1 lb		←→	
3.0 Coating Performance Evaluation and Materials Characterization		←→	
4.0 Delivery of 1-lb Batches of Coated Magnesium			←→

Task 1: Identify, Operate, and Optimize Equipment for Increased Batch Size

Task 1 encompassed the construction and testing of a scalable coating system capable of producing 1-lb batches of coated powder. This work was completed during the initial phase of this work and served as the basis for the scale-up work in the subsequent tasks.

Task 2: Scale-up of Batch Size to 1 lb for New Coating Process

Following the successful testing of the coating system with pure solvent and pure coating solution, the scale-up process was begun for coating atomized magnesium powder. Initial 100g batches of powder (-325 mesh atomized) were coated using coating parameters transferred from the smaller coating system used previously for laboratory coating in the previous phase II work. The coated powder was analyzed primarily by SEM in order to estimate coating quality and coverage as well as uniformity throughout the batch.

Although only small amounts of powder can be sampled in the SEM, effort was taken to obtain representative material for analysis. As seen below in Figure 1, initial batches of Mg powder that were coated did not exhibit the desired uniform coverage observed in previous lab-scale batches under similar parameters. Process changes were incorporated into subsequent batches to address these differences, and coating quality and uniformity were systematically improved.

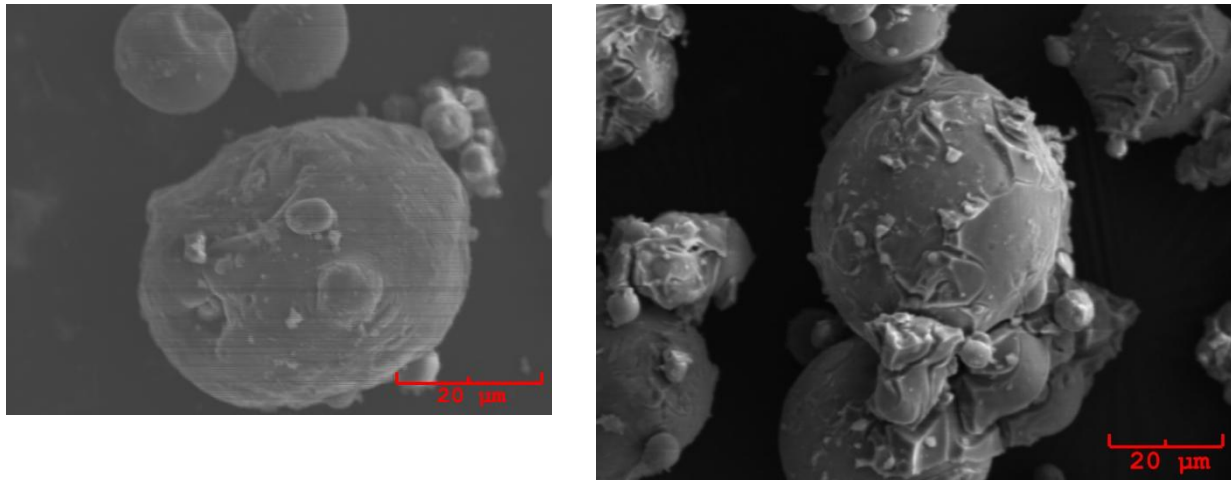


Figure 1: SEM images of magnesium powder coated in 100g batches with new coating procedure. The left image is representative of early coating runs typified by poor coverage of Mg powder. The image above right is typical of later runs with much better coverage of the Cerablak™ coating.

Following the initial assessment of the coating quality by SEM and EDS, coated powder batches were analyzed by nitrometer and TG/DTA to assess magnesium content of the coated powder, magnesium hydroxide content, and apparent barrier properties toward nitride formation at elevated temperature. As anticipated, the processing parameters for the coating of powder in the larger coating system required adjustment as the batch size increased in order to compensate for the coating vessel surface area and increasing demand on the heating and cooling systems. This process was repeated for each magnesium powder type to obtain proper process parameters necessary to achieve high coating quality.

Task 3: Coating Performance Evaluation and Materials Characterization

Characterization of initial 1-lb batches of as-coated powder

Particle Size

Due to the thin and highly conformal nature of the coating, the particle size distribution of the as-received powders is substantially retained in the coated powder. Powder specifications in terms of particle size are established through pass/retention statistics on sieves with particular mesh sizes. Although the precise distribution of the powder particle sizes was not compared, all coated powders in this work still passed through the sieve corresponding to the largest particle size in the as-received magnesium powder. This result confirms that there is no significant agglomeration in the powder, at least for the larger particles.

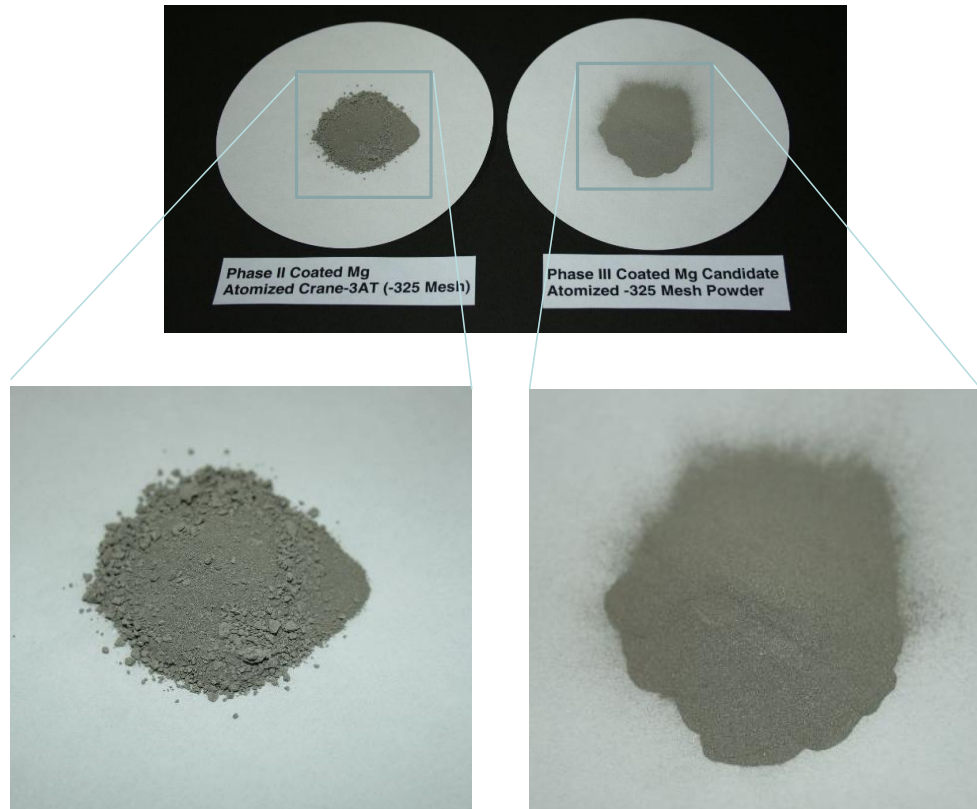


Figure 2: Coated -325 Mesh atomized powder produced during phase II (left) and phase III (right). Under equivalent post-processing, the current powder shows much less agglomeration and a finer texture.

Coating Quality

Criteria used to establish the coating quality for all powder grades was the visual indication of a coating in the SEM images and the identification of the Cerablak® elemental signature in EDS spectra obtained from various areas of the sample. Good coating coverage was identified for all four magnesium powder grades, as exemplified in Figure 3 for the -325 mesh atomized powder.

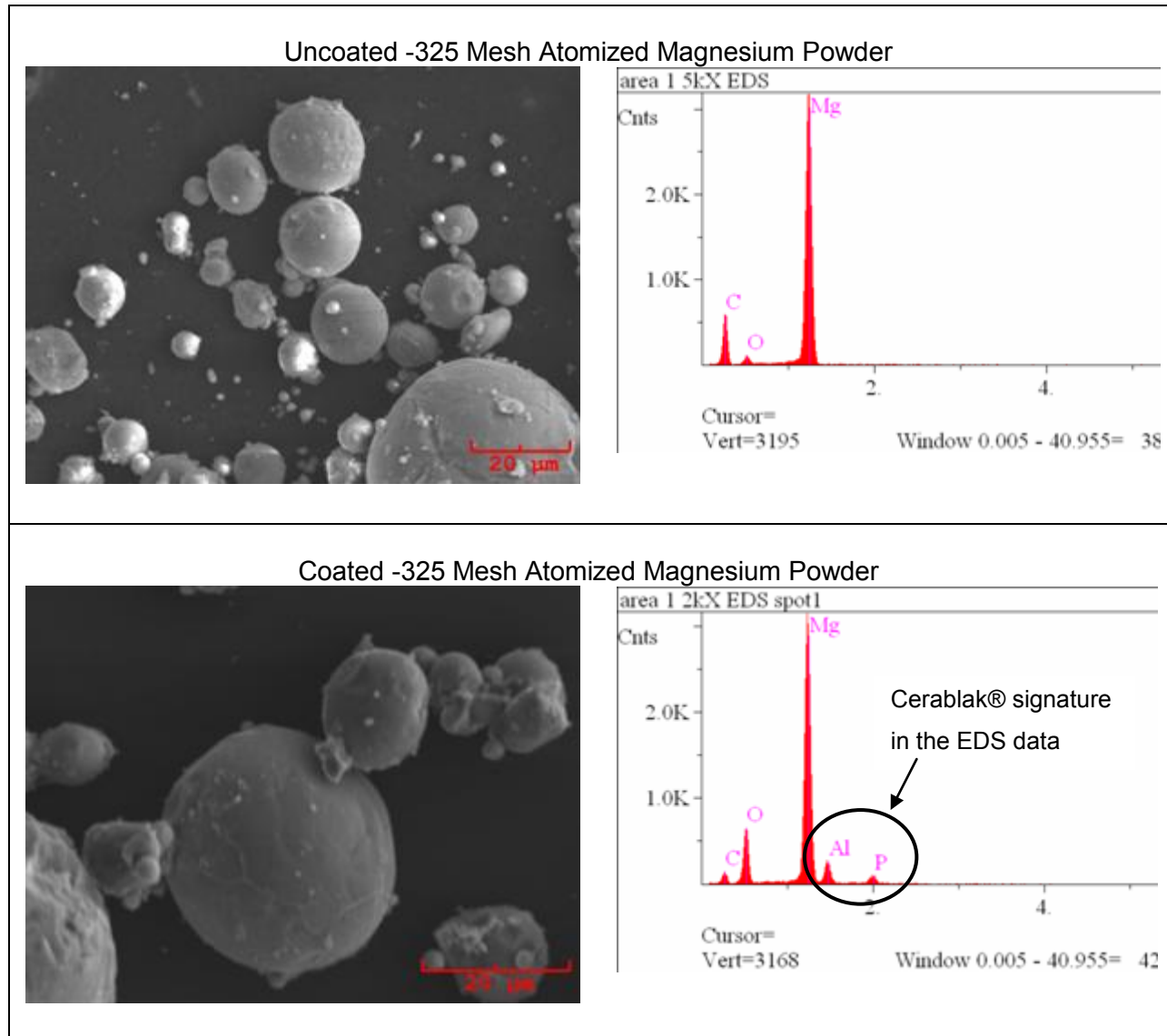


Figure 3: SEM and EDS results for coated versus uncoated -325 mesh atomized magnesium powder. Little change in the particle morphology is noted due to the conformal nature of the coating and uniform coverage; however, the characteristic signature of the Cerablak® coating is observed in the EDS spectrum indicating the presence of the coating.

Available Metallic Magnesium

Following confirmation of good coating coverage of the powder, additional testing was carried out in order to ensure that no significant reduction of metallic magnesium content occurred during the coating process. This analysis was carried out using a nitrometer; and although the accuracy of the nitrometer is only approximately $\pm 5\%$ in our laboratory configuration, comparison of as-received powder to as-coated powder could detect any substantial changes that occurred during the coating process. For the atomized magnesium powder grades, no statistically relevant degradation was observed. As discussed below, the analysis of the coated

ground powder showed a small decrease in available metallic magnesium which results from the different process used for coating of the ground powder.

Moisture-Induced Degradation

Overview

The performance of the Cerablak® coating as a barrier toward atmospheric moisture induced aging was tested for the initial 1-lb batches of coated powder. Samples were introduced into a controlled-humidity chamber which maintained conditions of 50°C/55%RH, and the powder was periodically tested by TGA in order to assess the magnesium hydroxide content of the aged powders. While this technique does not directly measure the metallic magnesium content of the powder, it is sensitive toward magnesium hydroxide formed during reaction between metallic magnesium and water vapor during aging. This technique was favored over nitrometer testing, which was used in the earlier Phase I and II work, due to the greater sensitivity.

Atomized Powder

Due to the relatively slow aging characteristics of some of these atomized powders under the aging conditions of 50°C/55%RH, aging of the initial 1-lb batches of coated powder was followed for two months. This period of time was considered sufficient to determine whether any negative influence of the coating on the aging process was observable before production of the required deliverable was initiated. For all powders tested, the measured degradation was the same as, or lower than, the uncoated powder of the same type. Due to the time required to complete this aging analysis, it was necessary to pursue a 3-month no-cost extension which was processed in December of 2007 and which moved the project completion date to April 6, 2008.

Based on the positive aging results for the initial 1-lb batches of each atomized powder type, production of the deliverable quantity of each powder was started.

Ground Mg Powder

Initial testing of the coated ground powder, RMC200BS, indicated poor performance during aging under accelerated conditions, which was consistent with the results obtained in the Phase II effort. Despite the reduced agglomeration of the powder produced using the new coating procedure, the aging performance showed an increased rate of moisture-induced degradation compared to the uncoated material.

Following these initial results, a significant research effort was focused on improving the performance of the 1-lb batches of ground Mg powder. As shown in Figure 4, the performance of coated ground Mg powder under accelerated aging conditions of 50°C/55%RH was improved dramatically compared to the performance of the powder from the previous Phase II project (Phase II powder is shown as coating variant 1). Because the degradation of uncoated ground Mg powder is rapid under our exposure conditions, 5 days of exposure was sufficient to gauge the performance of new coating variants.

The variant that was adopted for the production of the deliverable coated ground powder is shown as "Variant 5" in Figure 4. This variant allows for a small percentage of $\text{Mg}(\text{OH})_2$ in the as-coated material; however, it advantageously results in an extended period of stable performance as shown in Figure 5. Following longer exposure times at 50°C/55%RH, the period of stable performance eventually gives way to hydroxide formation, but the net result is performance that is much more stable initially and a resulting degradation that is significantly lower than that of the uncoated powder after about 7 days of aging. The approaches taken were successful in reducing the initial period of accelerated aging that was present in the Phase II powder. Although further performance improvement could be expected by continuing the approaches we took as well as optimization of coating quality, the impact of the coating on other relevant properties such as burn-rate, sensitivity to ESD and the like also should be considered when optimizing the coating. These properties will not be determined until after delivery of the first batches of powder to NSWC Crane at the conclusion of this project.

Progress in RMC200BS Coating Performance

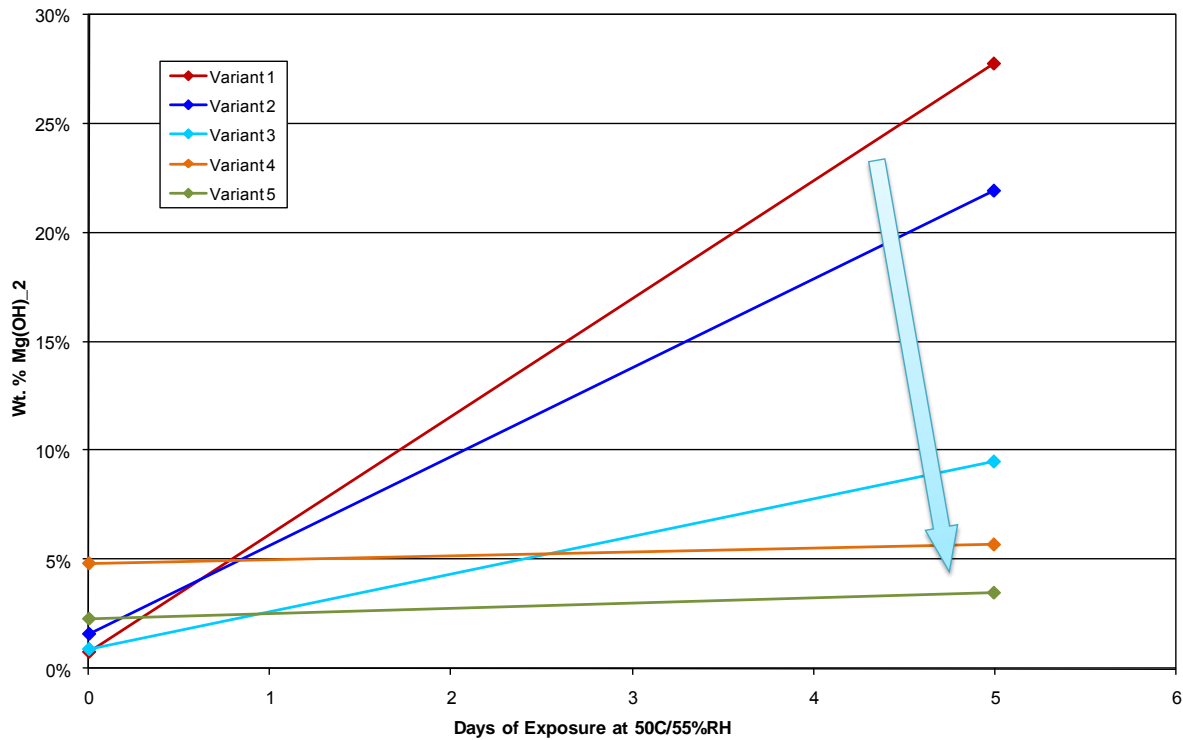


Figure 4: Magnesium hydroxide formation, as determined by TGA, for 5 coating variants on RMC200BS ground Mg powder before and after exposure to accelerated aging conditions of 50°C/55%RH. Coating variant 1 represents the performance of material produced during the Phase II project, and variant 5 represents the material produced under this Phase III project.

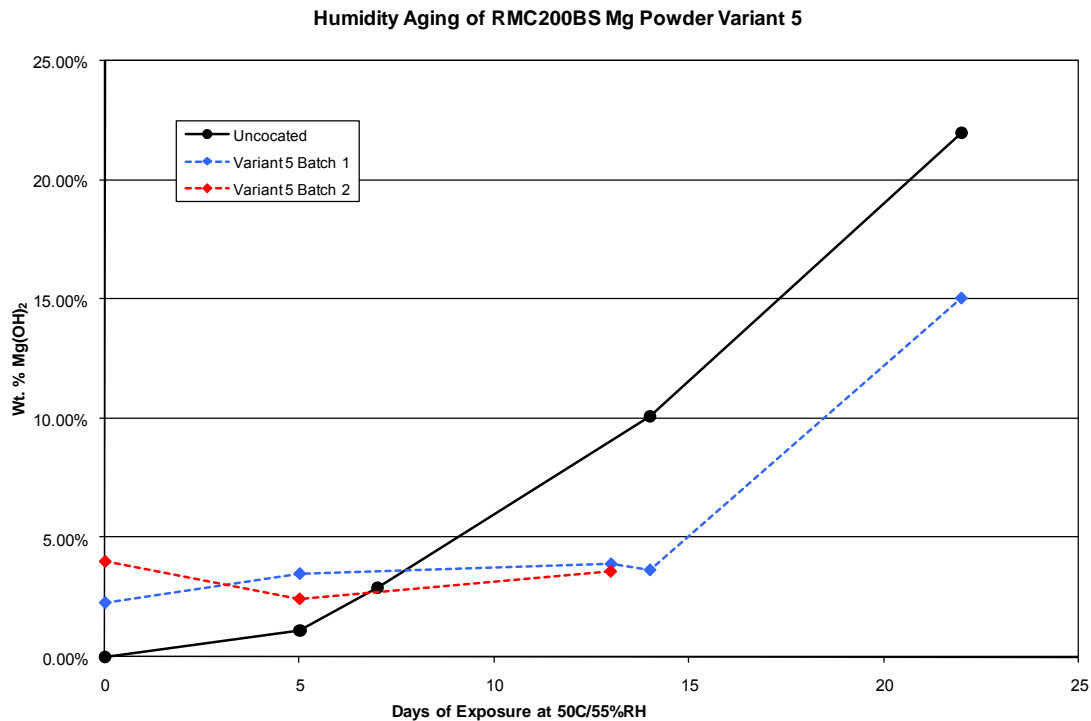


Figure 5: Magnesium hydroxide formation during exposure to accelerated aging conditions of 50°C/55%RH, as determined by TGA, for RMC200BS ground Mg powder coated using variant 5 as compared to uncoded powder of the same grade.

Characterization of Production 1-lb Batches

Characterization of the initial 1-lb batches of coated powder was used to establish baseline data for the specification and performance of the production batches of each powder type. Based on the baseline data and the coating parameters established in Task 2, the deliverable quantity of each type of magnesium powder was produced in 1-lb batches. The powder types were produced sequentially beginning with the atomized powders and ending with the ground powder.

Process parameters were carefully recorded during the coating process for each batch, and all anomalies were flagged for review. This provided for a high degree of reproducibility for the coating process itself. As-coated powders were tested via nitrometer for metallic magnesium content and by TG/DTA for magnesium hydroxide content. Significant deviation of those characteristics from those of the initial 1-lb batches indicated a problem with that production batch, and those batches were discarded from the final deliverable. This procedure resulted in a high degree of confidence in the reproducibility of the individual powder batches, and this reproducibility was reflected in the subsequent aging performance.

The final test criteria for the coated powder was the rate of degradation upon exposure to accelerated aging conditions of 50°C and 55%RH. As described previously, samples were introduced into the aging chamber and tested periodically for magnesium hydroxide content. The quantity of magnesium hydroxide after a given exposure time was compared to that of uncoated powder and the initial 1-lb batches of the same type. This process was carried out on every 3rd batch of powder produced, which provided a statistical measure of the performance of the entire deliverable. As seen from the data for the various powder types (see below), the aging performance of the batches was highly reproducible, and the statistical sampling of every 3rd batch provided reliable data for each powder type.

The above data was collected for each powder type and are included in Figure 8 to Figure 10 below. This data can be referenced to the deliverable powder batches through the powder type and batch numbers included for each 1-lb batch of powder delivered under this contract.

As-coated Characterization Data for Atomized Powders

As reported above, 1-lb batches of coated powder were analyzed by nitrometer for metallic magnesium content and by TGA for magnesium hydroxide content. Nitrometer analysis allows for the determination of metallic magnesium in a given sample through the production of hydrogen gas upon reaction with acid. Due to errors involved in the measurement that are dependent on the apparatus and the particular powder type, the accuracy of the data can vary significantly. The accuracy of the measurement for the fine-particle size powder was inherently better than that for the larger particle size powders as can be seen in Figure 6 below. For the -325 mesh and 200/325 mesh powders, it is estimated from this data that there is less than 5 wt% difference in the amount of metallic magnesium in the coated powder versus the uncoated powder, and approximately 3% of this weight difference can be accounted for by the Cerablak®-based coating. For the Gran 16 powder, the scatter in the data is quite large, and an accurate determination of metallic magnesium content is difficult due to the large scatter in the data; and it is useful to instead look at the TGA data for magnesium hydroxide content.

TGA analysis of the as-coated powders is a reproducible and accurate method for the determination of magnesium hydroxide content. This data for each of the deliverable 1-lb batches of atomized powder is shown below in Figure 7. The error inherent in the analysis when small quantities of magnesium hydroxide are present in a magnesium sample makes accurate determination below 1 wt% difficult; however, it can be seen from this data that the magnesium hydroxide content of the as-coated atomized powder batches lies below 1% [a

baseline error in the measurement of batch #5 of -325 mesh atomized powder is responsible for the high value seen in the figure, and subsequent analysis suggested a more reasonable value <1%].

The aging data shown in Figure 8, Figure 9, and Figure 10 for each of the atomized powder types shows the performance of the coated powder compared to the uncoated reference powder under the exposure conditions of 50°C/55%RH. All powders exhibited lower magnesium hydroxide content following a given exposure time than the uncoated powders, and the fine-mesh powders performed the best under the given conditions. In particular, the coated -325 mesh atomized powder aged at less than one half the rate of the uncoated powder of the same type.

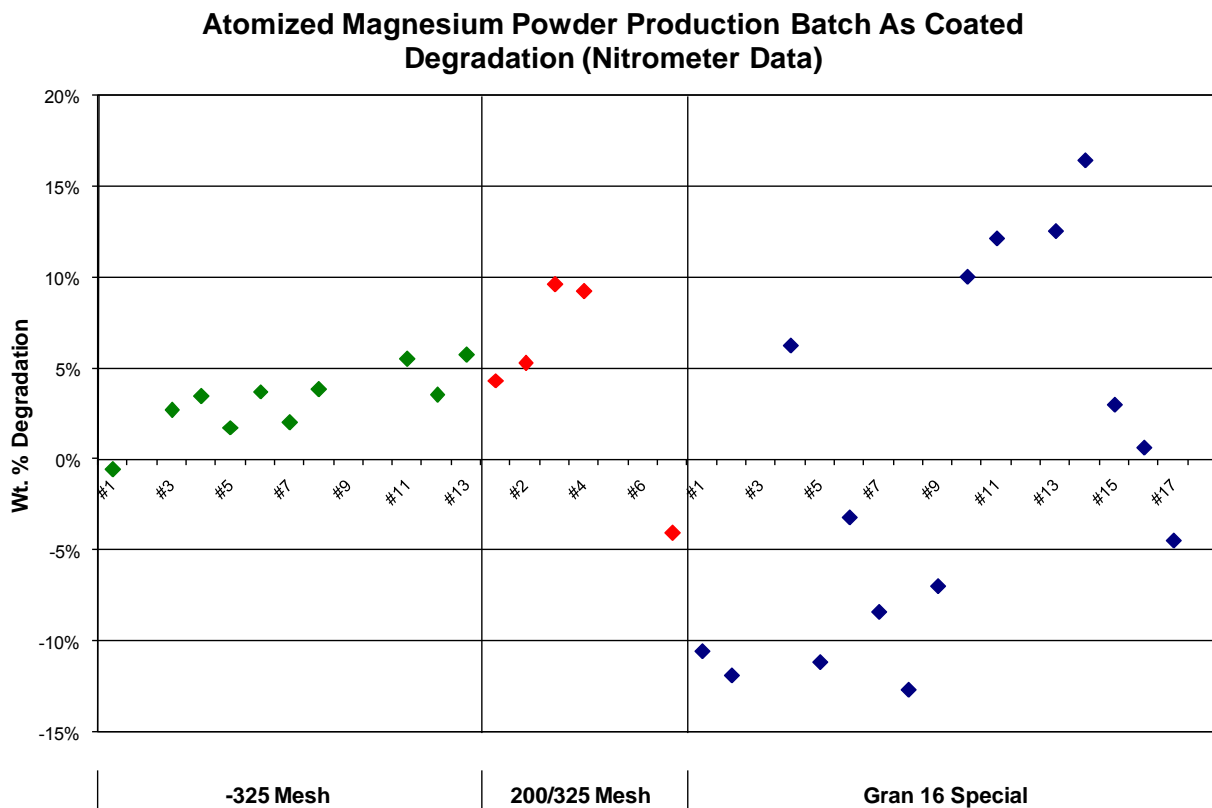


Figure 6: Nitrometer analysis of metallic magnesium content of coated atomized powders.

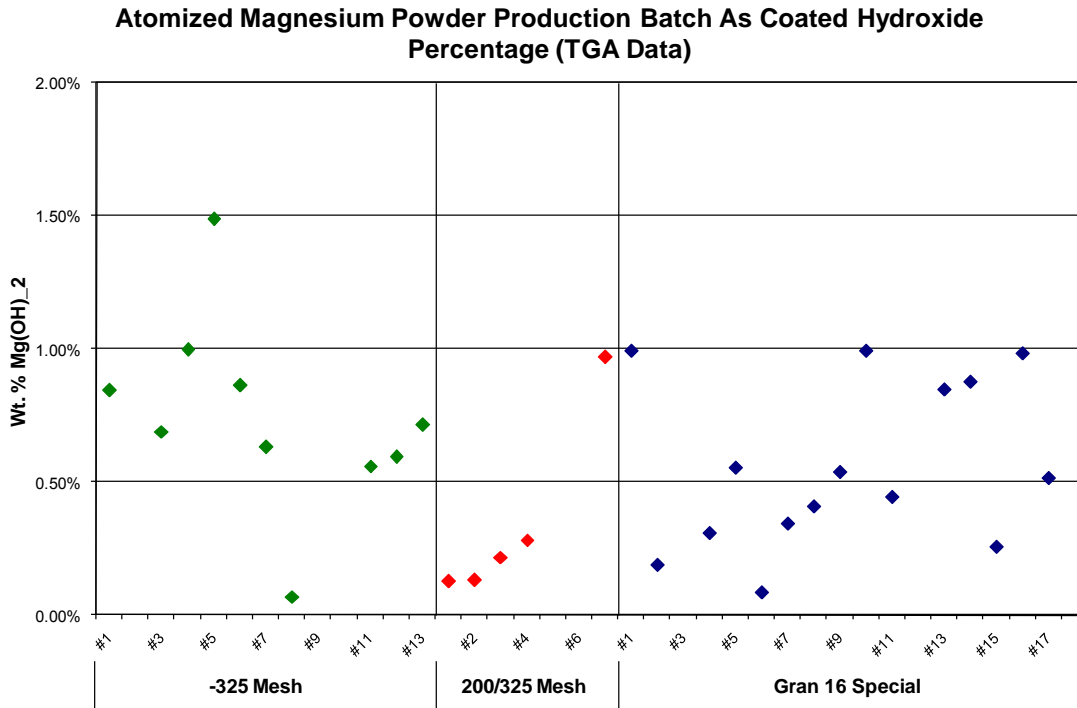


Figure 7: Magnesium hydroxide content as measured by TGA analysis for the 1-lb batches of as-coated atomized powder

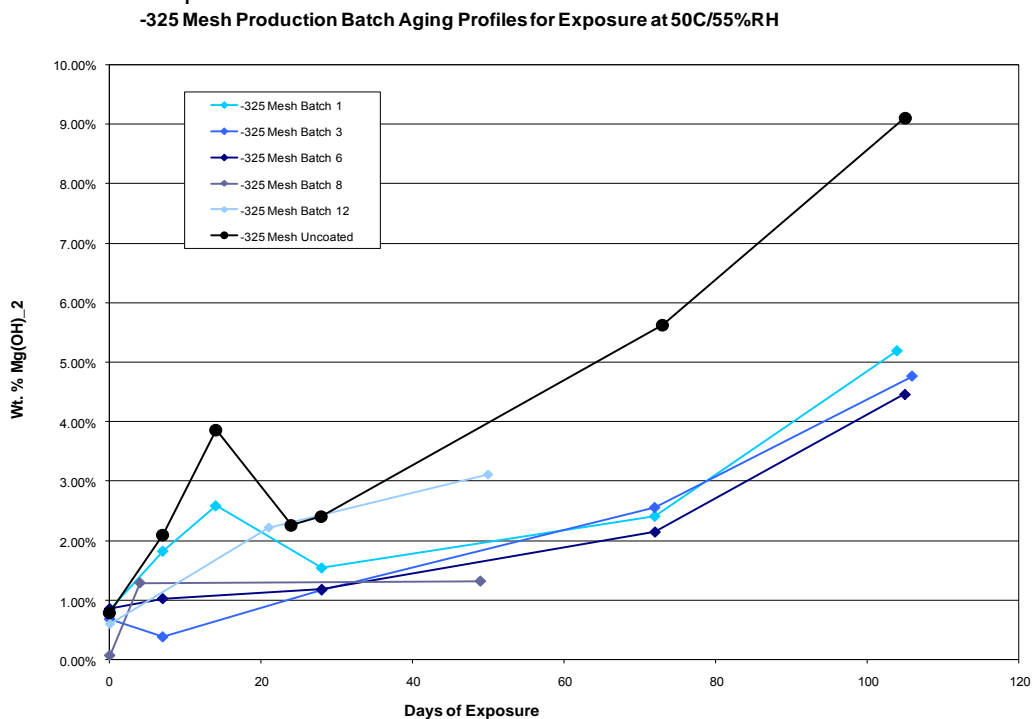


Figure 8: Magnesium hydroxide formation, as determined by TGA, for coated and uncoated - 325 mesh atomized Mg powder during exposure to accelerated aging conditions of 50°C/55%RH.

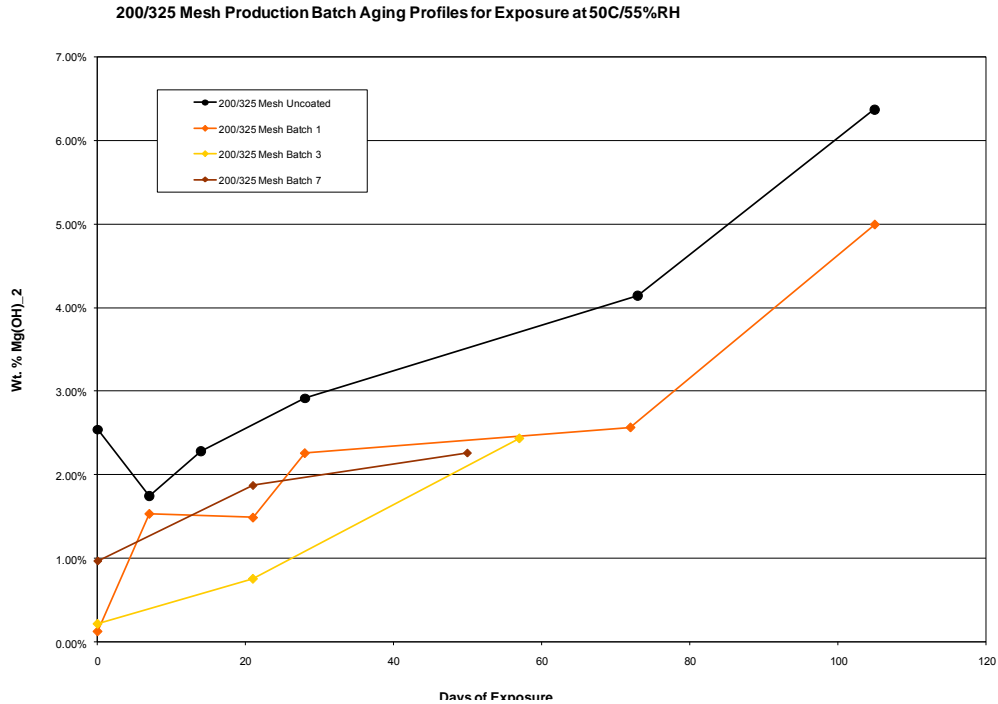


Figure 9: Magnesium hydroxide formation, as determined by TGA, for coated and uncoated 200/325 mesh atomized Mg powder during exposure to accelerated aging conditions of 50°C/55%RH.

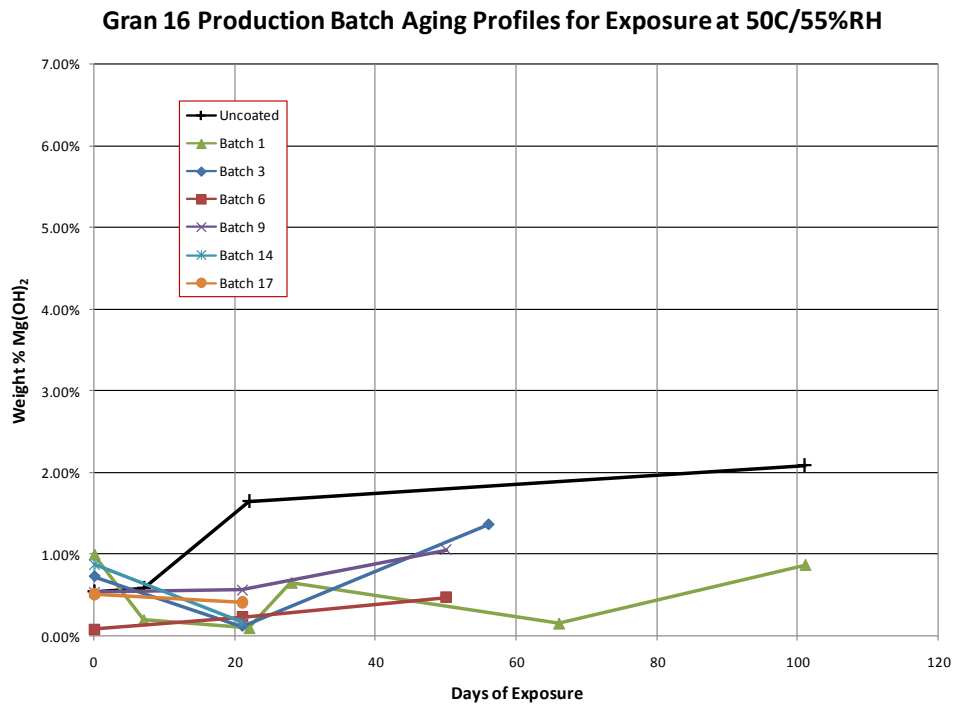


Figure 10: Magnesium hydroxide formation, as determined by TGA, for coated and uncoated Gran 16 atomized Mg powder during exposure to accelerated aging conditions of 50°C/55%RH.

RMC200BS Ground Powder, 25 1-lb Batches

Each 1-lb batch of coated RMC200BS ground magnesium powder was analyzed by nitrometer and TGA as described above for the atomized powder. As shown in

Figure 11 for TGA analysis of the as-coated powder, there is approximately 3wt% magnesium hydroxide present in the material due to the process variation compared with the atomized material. Although the hydroxide content is not desired, the resulting powder shows good stability in aging tests; and the hydroxide content is highly stable during exposure to humidity compared to uncoated powder which begins to form hydroxide rapidly on exposure to humidity.

Nitrometer analysis of the as-coated powder is dependent on good reference data for the baseline indicator for “zero” degradation, which was difficult to obtain for the ground powder. As a result, the zero point is not well known; and an estimate was used for reference. As shown in

Figure 12 below, there is approximately a 10% decrease in metallic magnesium by weight compared to uncoated powder based on this data. The 10% decrease seen in the nitrometer data is comprised of approximately 3% due to $\text{Mg}(\text{OH})_2$, 3-4% due to Cerablak®-based coating, and an estimated 1% MgO with the remaining 2% not determined; however, the 2% may be a result of the uncertainty in the reference of the zero point.

Performance of the coated ground powder compared to uncoated ground powder is shown in Figure 13 below. As can be seen in this figure, uncoated ground powder begins to develop magnesium hydroxide soon after exposure to the humid environment, and the rate of hydroxide formation increases with time during the analysis period shown in the figure. In comparison, the coated powder shows a long, stable region of performance during which little magnesium hydroxide is formed. After approximately 7 days of exposure, the magnesium hydroxide content in the uncoated material exceeds that of the coated material. Performance beyond 14 days shows somewhat variable behavior, and this behavior appears to be highly dependent on processing conditions. It is expected that further improvement in the extended aging performance can be achieved through further coating optimization.

Although the 3 wt% magnesium hydroxide found in the as-coated ground powder is undesirable, it results in highly stable performance over an extended period of time, which likely will result in increased shelf-life compared to uncoated powder. This is highly advantageous compared to uncoated powder which degrades quickly upon exposure to humidity.

RMC200BS Production - As Coated TGA Data

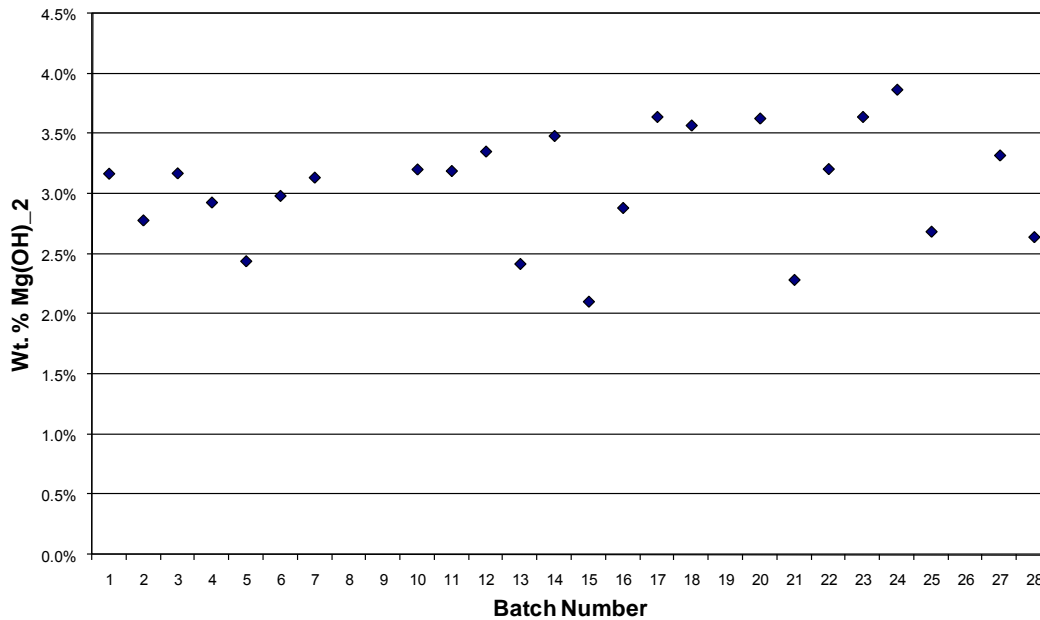


Figure 11: Magnesium hydroxide content as measured by TGA analysis for the 1-lb batches of as-coated ground powder

RMC200BS Production - As Coated Nitrometer Data

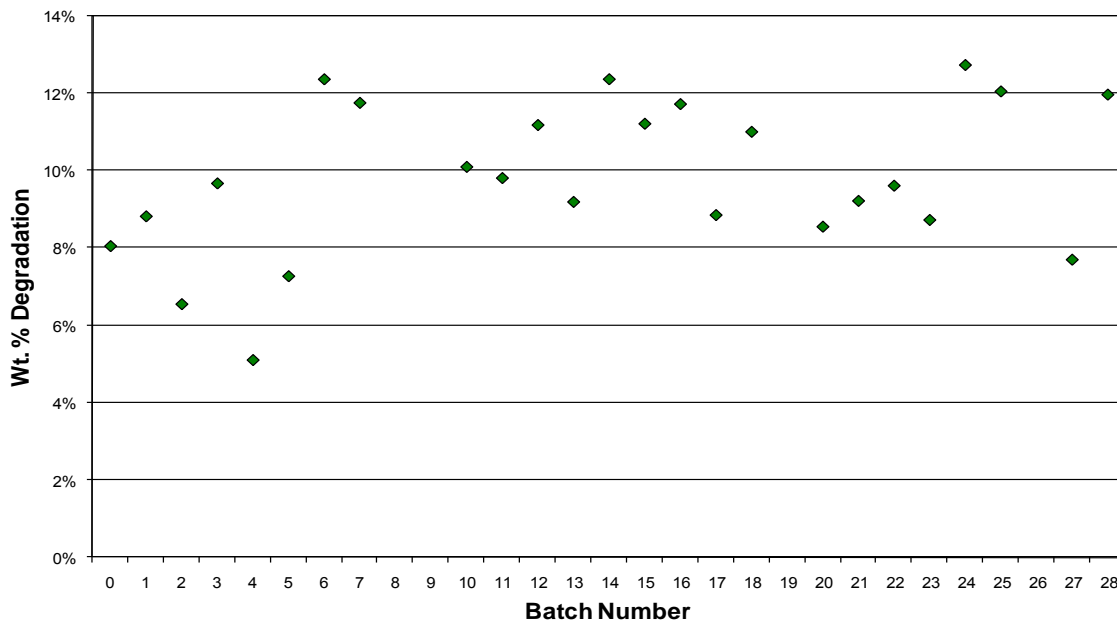


Figure 12: Nitrometer analysis of metallic magnesium content of coated ground magnesium powder RMC200BS.

Cerablak Coated RMC200BS Mg Powder Humidity Aging Profiles

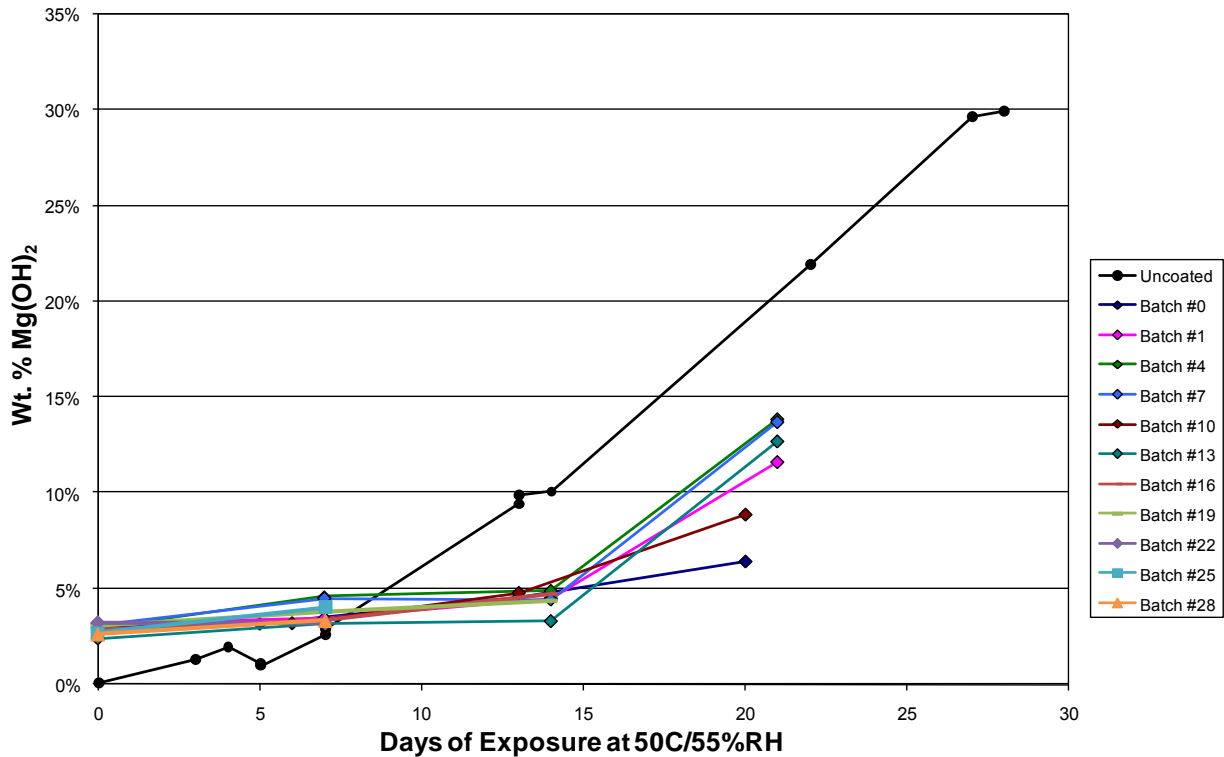


Figure 13: Magnesium hydroxide formation, as determined by TGA, for coated and uncoated RMC200BS ground magnesium powder during exposure to accelerated aging conditions of 50°C/55%RH.

Task 4: Delivery of 1-lb Batches of Coated Magnesium

As described previously, deliverable batches of coated magnesium were selected based on the adherence of production parameters to specified norms, characterization of as-coated powder for metallic magnesium and magnesium hydroxide content, and aging performance under conditions of elevated temperature and humidity. Selected powder batches were packed in individual conductive bags, sealed, and marked with the powder type and batch number. For shipping, the individual 1-lb bags of coated powder were packed in steel pails, sealed, and marked for delivery. The final shipment consisted of 1 pail containing all 30 1-lb batches of atomized powder and 1 pail containing all 25 1-lb batches of ground powder.

Tables detailing powder quantities and batches contained in the final shipment are included below (see Table 2 and Table 3).

Table 2: Magnesium powder type and number of 1-lb batches contained in the final deliverable shipment

Material Type	# of 1lb. batches
Atomized, Gran 16 Special	15
Atomized, -325 Mesh	10
Atomized 200/325 Mesh	5
Ground, RMC-200-BS	25

Table 3: Powder Batch Numbers Included in the Final Deliverable

Powder Batch Numbers For Final Deliverable				
-325 Mesh Atomized	200/325 Mesh Atomized	Gran 16 Atomized	RMC200BS Ground	
1	1	1	0	17
3	2	2	1	18
4	3	4	2	20
5	4	5	3	21
6	7	6	4	22
7		7	5	23
8		8	6	24
11		9	7	25
12		10	10	27
13		11	11	28
		13	12	
		14	13	
		15	14	
		16	15	
		17	16	